Lane formation in driven colloidal mixtures: is it continuous or discontinuous?

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Binary mixtures of oppositely charged colloids driven by an electric field are shown to exhibit a nonequilibrium transition towards lane formation if the driving force is increased. Brownian dynamics computer simulations and real-space experiments are employed to study hysteresis effects in an order parameter measuring the extent of lane formation upon increasing and decreasing the driving force. Both from simulation and experiment, we find that lane formation due to electrical fields is continuous. However, simulations show a discontinuous transition if the driving force is gravity.

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In equilibrium, there is a fundamental difference between a sharp phase transition which exhibits a jump in a certain derivative of the free energy with respect to a thermodynamic variable [1] and a continuous crossover where no such discontinuity exists in the thermodynamic limit. This is much less clear for nonequilibrium phase transitions since a free energy does not exist in general in nonequilibrium. Here, in many situations, an order parameter can still be defined in the steady state and hysteresis behaviour typically serves as a criterion to discriminate between discontinuous and continuous behaviour [2]. While it is by now well-understood how the order of an equilibrium phase transition is controllable by the interparticle interactions [3, 4], the question of which key parameters determine the existence and order of nonequilibrium phase transitions is much less understood **due to the multitude** of parameters characterizing the **nature** of the dynamics which do not apply in equilibrium.

Lane formation in a binary mixture of Brownian particles which are driven by a constant external force depending on the particle species [5] represents a prototype of a nonequilibrium transition in a continuous (i.e. off-lattice) system [6]. Brownian dynamics computer simulations strongly support the scenario that for increasing driving force the system undergoes a transition from a mixed steady state towards a steady state where macroscopic lanes are formed. Such a laning transition has been found in models for oppositely driven repulsive mixtures [5, 7, 8, 9, 10, 11] in two and three spatial dimensions. In two spatial dimensions, it was found [5] that a suitable order parameter which detects laning exhibits a significant hysteresis - if the driving force is increased and subsequently decreased - which signals a discontinuous nonequilibrium phase transition. This issue is still unclear in three spatial dimensions. Though the general scenario occurs for pedestrian dynamics [12, 13], in driven granular [14, 15] and colloidal [16] matter and in complex plasmas [17], a quantitative comparison of laning with simulation data and the determination of the underlying order of the transition is still lacking.

The aim of this letter is twofold: first, we show that oppositely charged colloidal particles driven in an electric field [16] exhibit lane formation in quantitative agreement with our Brownian dynamics computer simulations. Second, we address the question whether the transition towards lane formation is discontinuous or a smooth crossover. While charged colloids are found to exhibit lanes in a continuous way upon increasing the electric field strength, additional simulations reveal that the transition becomes discontinuous if gravity is the driving force. The physical reason is that hydrodynamic interactions are screened in the electric context [18, 19] while they are long-ranged for gravity. In fact, three-dimensional simulations which neglect hydrodynamic interactions completely yield a continuous transition as well. Our results demonstrate that the existence and order of a nonequilibrium phase transition depends on details of the dynamics even when the particle interactions which entirely determine the order of phase transitions in equilibrium are kept fixed.

In our experiments, we used suspensions of polymethylmethacrylate colloids in a density matching mixture of cyclohexyl bromide and cis decalin into which we dissolved 60 μM tetra butyl ammonium bromide salt. An equimolar binary suspension of colloids fluorescently labelled with Rhodamine and 7-nitrobenzo-2-oxa-1,3-diazol with volume fraction $\eta_N = \eta_R = 0.1$ was prepared. The diameter of both species was 1.2 μm. The inclusion of salt led to both colloidal species accquiring opposite charges of $Z_i = 100$e, and a Debye screening length of $\kappa^{-1} \approx 300$ nm [16]. The solvent dielectric constant ϵ was 5.5, and shear viscosity was $\eta = 2.2$ cP. All experiments were conducted at room temperature $T = 300$ K. We used a Leica NT confocal laser scanning microscope. Experimental data was taken in 2D scans of

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typically 100 μm in width at a frame rate of around 2 **frames per second**, ie coordinates were collected from a diffraction-limited slice of $\sim 2\mu m$ in depth.

In our Brownian dynamics computer simulations, we consider an equimolar binary mixture of $N = 1024$ oppositely charged colloidal particles of hard-core diameter σ at corresponding total volume fraction $\phi = 0.2$ dispersed in a solvent whose viscosity and dielectric constant matched the experimental values, likewise we set and $T = 300$ K.

The simulation is performed in a cubic box of length l with periodic boundary conditions in all three directions [20]. Apart from their steric repulsion, the particles interact via the screened Coulomb potential

$$V_{ij}(r) = \frac{Z_i Z_j}{\epsilon(1+\kappa\sigma/2)^2} \frac{e^{(-\kappa\sigma(r/\sigma-1))}}{r} \tag{1}$$

where i and j label the particle species, Z_i denotes the particle charge, r is the interparticle separation and κ is the inverse Debye-Hückel screening length depending on the salt concentration in the solvent. We take $\kappa\sigma = 4$ in order to match the experimental salt concentration. An electric field $\vec{E}$ yields the driving forces $\mathbf{F}_i^{\mathrm{ext}} = Z_i^* \vec{E}$ acting on the particles. The actual electrophoretic charge renormalization is taken to be $Z_i^*/Z_i = 0.8$ as obtained from the averaged drift velocity in the electric field at low densities [21].

Time-dependent trajectories of the particles are calculated using a finite-time step method with a configuration-dependent diffusion tensor [22]. The magnitude of friction is set by the Stokes-drag expression where the free diffusion constant is given by $D_0 k_B T/3\pi\eta\sigma_H$ (with k_B denoting Boltzmann's constant) which sets the typical Brownian time scale $\tau_B = D_0/\sigma^2$. Here the hydrodynamic diameter of the particles is set very close to the interaction core σ such that $\sigma_H = 0.98\sigma$. We use the pairwise approximation based the Long-Ajdari mobility tensor [18] in order to include hydrodynamic interactions properly for a driving electric field [19]. After an initial relaxation period of typically $20\tau_{\mathrm{B}}$ the system runs into a steady state. The time-step used in the simulation was $\Delta t = 10^{-4}\tau_B$.

Experimental snapshots in the steady state for two electric field strengths $E = 30kV/m$ and $E = 100kV/m$ are presented in Figure 1. The vertical extent of the optical slice is set by diffraction, leading to a lengthscale of order $2\mu m$. The snapshots clearly reveal the onset of laning for increasing electric driving field. Corresponding snapshots of our Brownian dynamics computer simulations are presented in Figure 2. For sake of comparison, the same field strengths were used as for the experimental snapshots. The simulation configurations show a similar tendency towards laning along the drive direction when the electric field is increased.

In order to quantify the extent of laning, we define a laning order parameter m as follows: we assign a cylinder of diameter 0.9σ and total height 6σ symmetrically around the center of each particle i such that the cylinder axis is parallel to the driving field. If one or more particles of different species are contained in this cylinders, we define the value of $m_i = 0$ to this particle while $m_i = 1$ if the cylinder is free from other particles with an opposite charge. The averaged dimensionless laning order parameter

$$m = < \sum_{i=1}^{N} m_i > /N \tag{2}$$

where $< \ldots >$ refers to a particle and steady-state average and N is the total number of particles considered

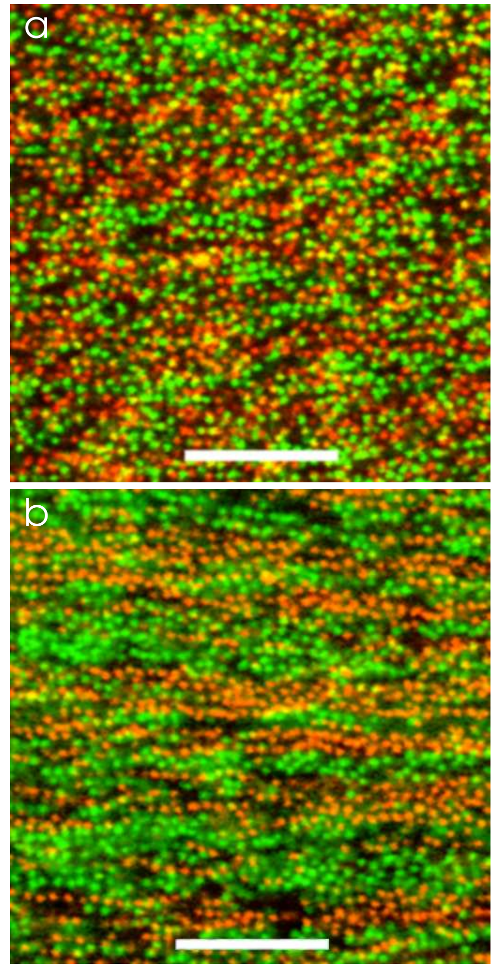

FIG. 1: Typical particle configuration for positively (green spheres) and negatively (red spheres) charged colloids in an electric field of strength E along the horizontal direction. Only particles whose centres are within a slice of thickness $2\mu m$ are shown. The length bar is 10 μm. The formation of lanes can clearly be seen. (a) experimental snapshot for $E = 30kV/m$, (b) experimental snapshot for $E = 100kV/m$. The other parameters are given in the text.

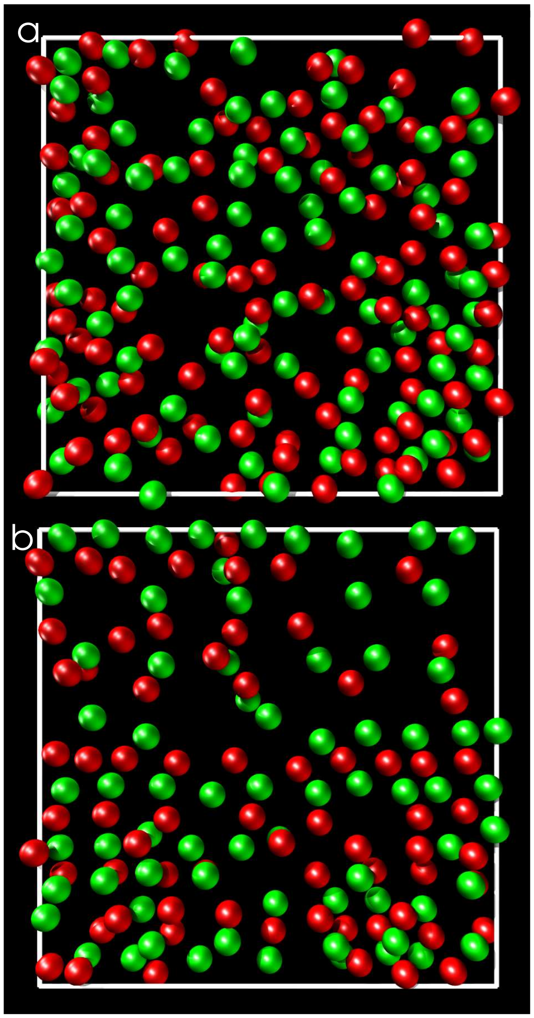

FIG. 2: Computer simulation snapshots for positively (green spheres) and negatively (red spheres) charged colloids in an electric field of strength E along the horizontal direction. Only particles whose centres are within a slice of thickness 2σ are shown. (a) $E = 30kV/m$, (b) $E = 100kV/m$. The other parameters are given in the text.

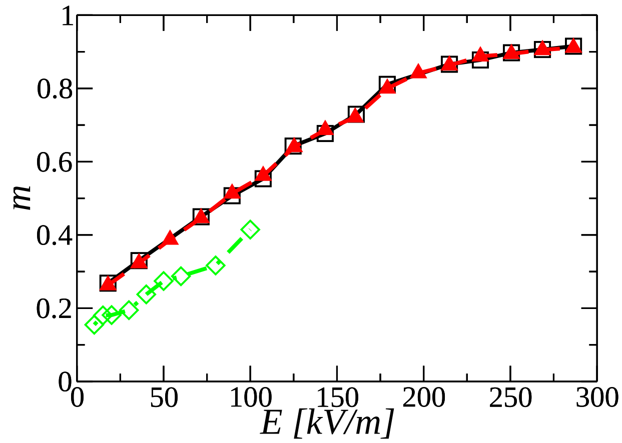

FIG. 3: Averaged laning order parameter m versus electric field strength E (in units of kV/m). The open squares (full line) are the simulation results upon increasing the field strength, the full triangles (dashed line) shows the same upon decreasing the field strength. No hysteresis is found. The diamonds (dot-dashed line) are the experimental data. The parameters are the same as in Fig. 1.

measures the averaged extent of laning. By construction, the laning order parameter m equals 1 if particles of the same species are always on top of each other along the drive but it vanishes in a completely mixed situation. We have averaged this laning order parameter over many simulation configurations. For the experimental data, a similar laning order parameter was obtained by using a projected cylinder (i.e. a rectangular cut) to the plane containing the particles. Plots of the laning order parameter m versus the strengths of the electric field applied are presented in Figure 3.

First, there is reasonable agreement between simulation and experiment. The increase of the laning order parameter with the external drive is smooth. The experimental data reveal a slightly smaller laning order parameter than the simulation which is acceptable given the uncertaincy in the particle charge. The experimental data were taken both increasing and decreasing the external field, and no difference was observed. Hence we conclude that effects of hysteresis are largely absent. We remark that possible effects arising from electro-osmotic flow are not exactly known.

Finally, we consider the case of gravity in which the driving forces result from a different buoyant mass of the two particle species. In particular, we treat the symmetric case here where plus and minus charged particles feel the same gravitational force but just their sign is different. Our Brownian dynamics computer simulations are now performed with the unscreened Rotne-Prager mobility tensor [23] replacing the screened Long-Ajdari tensor. All the other parameters are kept unchanged. In Figure 4 the simulation results for the laning order parameter are shown for increasing and decreasing driving forces. The results are compared to the case of an electric field where the mobility tensor is screened due to counterion counter-motion. A significant hysteresis behaviour is detected for sedimentation which clearly signals a discontinuous transition towards laning while no such hysteresis is present for electrophoresis and in the complete absence of hydrodynamic interactions. This clearly indicates that it is the range of hydrodynamic interactions which make lane formation discontinuous. In a strictly two dimensional system, laning occurs in a discontinuous way even when hydrodynamic interactions are ignored completely [5]. Therefore besides the hydrodynamics the system dimensionality plays an important role in determining whether laning is discontinuous or continuous.

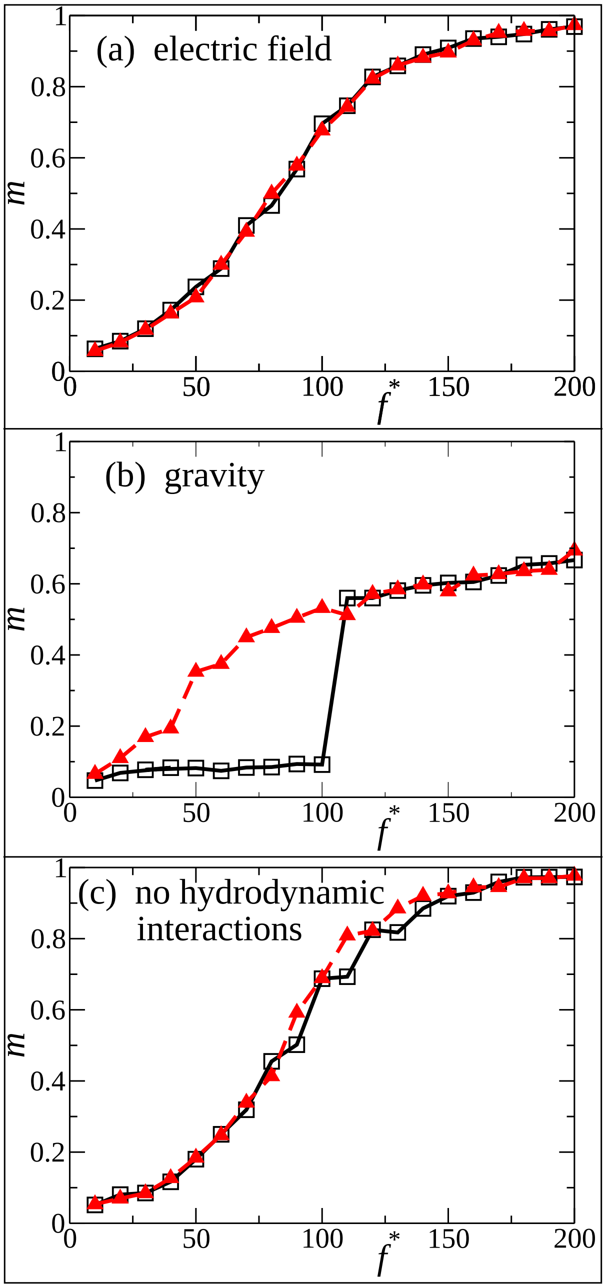

FIG. 4: Averaged laning order parameter versus reduced driving force f^* both upon increasing (open squares, full line) and decreasing (full triangles, dashed line) the driving forces: (a) for an electric driving field where $f^* = E \mod Z_1^* \mod \sigma/k_BT$ and hydrodynamic interactions are screened, (b) for a gravitational force Mg where $f^* = \pm Mg\sigma/k_BT$ and hydrodynamic interactions are long-ranged, (c) same as (a)/(b) but for neglected hydrodynamic interactions. The length of the cylinder in the definition of the order parameter here spans the whole simulation box.

In conclusion, we have shown that oppositely charged colloids driven by an external electric field show a continuous tendency towards lane formation if the driving strength is increased. Real-space experimental data are in quantitative agreement with Brownian dynamics computer simulations which include the screened hydrodynamic interactions between the driven colloids. The continuous crossover towards laning is in marked contrast to sedimenting colloids where lane formation occurs via a nonequilibrium first-order phase transition as revealed by a significant hysteresis behaviour in a suitable order parameter. This change must be attributed to the long-range nature of hydrodynamic interactions in the sedimentation case. In a reduced system dimensionality, on the other hand, laning is discontinuous as well even when hydrodynamic interactions are ignored. Hence the order of the lane formation is determined by both, hydrodynamic interactions and system dimensionality. Therefore the more general conclusion is that the existence and order of a nonequilibrium phase transition depends on details of the dynamics even when the particle interactions which entirely determine the order of phase transitions in equilibrium are kept fixed.

Lane formation does not only occur in colloidal systems but also in dusty plasmas where hydrodynamic interactions are absent but inertia effects play a dominant role [17]. We expect that, in three dimensions, the tendency towards lane formation will be continuous there as well. In strict two dimensions, e.g. for pedestrian dynamics and shaken granular matter, we expect a continuous behaviour irrespective to the details of the dynamics.

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